Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

indicated by Dimroth's reasoning, although no evidence of a direct nature was adduced and only the reactions of the mercury were considered in assigning the formula. It seemed to the writers that a study of the amino group in these compounds would furnish more direct evidence as to the structure than any at hand, for, obviously, a compound of the formula (I), where R = H, could not undergo the reactions characteristic of the primary amino group. This work was therefore undertaken as a preliminary phase of a more extended study of the mercuriated aromatic amines. It was found possible to prove formula (II) for *p*-aminophenylmercuric acetate by demonstrating the presence of the primary amino group in two ways: (1) the formation of a salicylidene derivative; (2) the ready formation of a diazo solution, from which were prepared the azo dyes with dimethylaniline, diethylaniline, phenol, resorcin, and α-naphthylamine-5-sulfonic acid. It was also found possible to prove the monomolecular structure of *p*-methylaminophenylmercuric acetate by demonstrating the presence of a secondary amino group through the preparation of the nitroso derivative. A more detailed discussion and a description of the compounds prepared will appear in the *Journal of Biological Chemistry*.

[1] *Zs. anorg. Chem.*, 32, 227 (1902).

[2] *Berlin, Ber. D. Chem. Ges.*, 35, 2038 (1902); *Zs. anorg. Chem.*, 33, 311 (1902).

MOLECULAR REARRANGEMENTS OF TRIPHENYLMETHANE DERIVATIVES. I. GENERAL DISCUSSION

By Julius Stieglitz

KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO

Read before the Academy, December 9, 1914. Received, February 20, 1915

Introduction.—In most chemical actions taking place at moderate temperatures, a change affecting an atom or a group of atoms in a molecule leaves the remaining atoms in undisturbed relations to one another. This stability of groupings of atoms led, especially in the domain of organic chemistry, to the theory of the structure of molecules and underlies our methods for determining these structures. Occasionally, however, the study of the product of a reaction shows that a profound rearrangement of the grouping of atoms in a reacting molecule has taken place. Molecular rearrangements of this kind are of special interest for the reason that their study should shed some light, from a purely chemical side, on the forces holding atoms in place in molecular structures. The evidence thus obtained should aid in the study of these forces by purely physical means.

The recent development of electron theories of valence has given the investigation of the causes underlying molecular rearrangements an opportunity for much greater precision in formulating the problems and in expressing the results of their study. Thus, the original electron theory of valence proposed by J. J. Thomson[1] has been used with advantage in interpreting the molecular rearrangements of hydroxylamine and halogen amine derivatives of certain organic compounds independently and practically simultaneously by L. W. Jones[2] and myself.[3] These interpretations differed in some important particulars, but agreed as to the fundamental relations.

The electron theory will here be used in expressing the results of recent investigations of molecular rearrangements of triphenylmethane derivatives. Inversely, certain definite conclusions may be drawn from the study of the rearranging compounds in regard to assumptions made in the various theories of valence; and it is proposed to present this evidence first as a contribution to the greater problem of valence from the field of pure organic chemistry—the very field in which newer views are most urgently advanced by physicists and physical chemists.

The Electron Theories of Valence and the Molecular Rearrangements of Halogen Amines and Similar Derivatives. When an acyl halogen amine R.CO.NH(Hal) is treated with bases, it undergoes the Hofmann rearrangement, the radicle R (which represents an alkyl or acyl radicle or hydrogen) being torn from its union with carbon and carried to the nitrogen.[4] We have, for instance:

$$R.CO.NH(Cl) + NaOH \rightarrow NaCl + HOH + CO{:}NR. \qquad (1)$$

Triphenylmethyl halogen amines, we have found,[5] undergo the same kind of rearrangement:

$$(C_6H_5)_3C.NH(Cl) + NaOH \rightarrow NaCl + HOH + (C_6H_5)_2C{:}NC_6H_5 \quad (2).$$

Now, in both these classes of chlorine derivatives, the chlorine unquestionably is present as the specific radicle Cl of hypochlorous acid:[6] for the compounds are prepared from hypochlorous acid; they form the acid by hydrolysis; they form hypochlorous esters with alcohols, hypochlorous amides with amines; in all of these reactions the specific oxidizing power of the hypochlorous acid radicle remains intact; all attempts to replace the chlorine atom by negative groups (OH, OR, NH_2) have proved futile; all attempts to prepare chloroamines by means of the hydrogen chloride radicle Cl and its derivatives (HCl, PCl_3, etc.) have likewise proved ineffectual. On the other hand, in compounds such as the alkyl chlorides $R_3C.Cl$ and acyl chlorides R.OC.Cl, the chlorine is unquestionably present as the specific hydrogen chloride radicle Cl: the compounds are prepared from hydrogen chloride or its derivatives (PCl_3, etc.); they form hydrochloric acid by hydrolysis, by treatment with ammonia and a variety of other reagents; the chlorine can be readily replaced by a great number of negative radicles; and in these chlorides, the chlorine has no oxidizing power.

There is, evidently, a fundamental difference in the condition of the halogen in these organic compounds, the rearranging chloroamines and the (non-rearranging) alkyl and acyl chlorides. This difference is sharply and precisely expressed in terms of Thomson's original theory of electron valences by the electron structure (Cl^+) for the hypochlorous acid radicle,[7] the positive charge indicating that the atom has lost an electron, and by the structure Cl^- for the hydrochloric acid radicle, the negative charge being due to an electron captured by the atom. The chloroamines then have the structure $R_2N^{-+}Cl$, the alkyl and acyl chlorides, the structures $R_3C^{+-}Cl$ and $R.OC^{+-}Cl$. (Here and throughout these articles only the valences in question are indicated.) These electronic structures give a complete and exact history of all the striking characteristics of the two groups of compounds, as just enumerated.

According to the more recent suggestions of J. J. Thomson,[8] the valences holding atoms in molecules, especially in the case of non-electrolytes, may be formed, not only in the fashion assumed in his original theory (called now 'intramolecular ionization'), but also by the electrical attraction between the normal electrons of one atom and the 'positive core' of the other, each atom remaining, as a whole, electrically neutral. Practically the same suggestion (following one made by A. A. Noyes[9] in 1907 that we might have two kinds of molecules of one and the same compound, as, for instance, HCl and H^+Cl^- for hydrogen chloride) had previously been made by Bray and Branch[10] and by G. N. Lewis,[11] who speak both of 'non-polar' valences as uniting atoms, especially in non-electrolytes, and of 'polar' valences, of the type assumed in Thomson's original theory. Thomson defined and elaborated more precisely than did the American chemists the nature of 'non-polar' valences. Both Lewis and Thomson consider that the valences may be polar in one part, non-polar in another part of the same molecule. (The terms non-polar and polar will here be used as signifying the two kinds of valence postulated also by Thomson's later theory, inasmuch, as they are much more convenient than the terms 'intra-molecularly ionized' and 'non-ionized' valences.)

It is evident, from the development given above, that even according to these newer views of valence, the electronic structure of the chloroamines, as far as the chloroamino radicle is concerned, must be a *polarized* one, $R_2N^{-+}Cl$ and not the non-polarized union $R_2N\rightleftarrows Cl$ permitted by the new theories, and that, similarly, the electronic structures of the alkyl and acyl chlorides should be considered polar, $R_3C^{+-}Cl$ and $ROC^{+-}Cl$. The non-polar structures $R_2N\rightleftarrows Cl$ and $R_3C\rightleftarrows Cl$ would not account at all for the persistent, fundamental differences in the properties of the chlorine in the two series of derivatives. Now, while both the chloroamines and the alkyl and acyl chlorides may be minutely ionizable, they certainly are not electrolytes in the ordinary acceptance of the term. We thus find that strongly polarized combinations of atoms need not produce electrolytes. This being the case in an instance open to demonstration, one is led inevitably to the inquiry, why it should not be true for a great many polarized combinations and whether the assumption of non-polar unions is at all necessary.

Very strong, if not so obvious, evidence, leads to the conclusion that the relations developed for the chloramines and the alkyl chlorides are duplicated by other series of compounds, for instance by the hydroxylamines[12] and the alcohols, whose relations may be expressed precisely and completely only in the polar structures $R_2N^{-+}OH$ and $R_3C^{+-}OH$. Again we have no exhibition of markedly basic properties by the alcohols (which form oxonium salts with acids and are 'base-forming' like ammonia, but not bases, ionizing directly simply as weak acids) in spite of the strong evidence of intramolecular ionization.

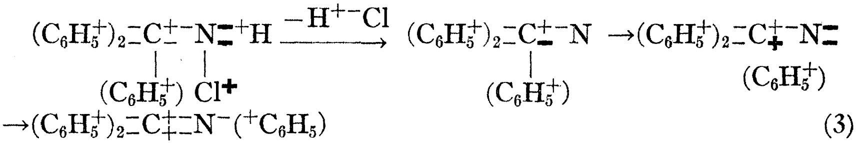
Finally, it should be said in this connection, that exactly the same persistent fundamental differences as exist between positive and negative chlorine in organic compounds are clearly manifested between nitrogen as the nitrous acid radicle N^{+++}, say in the diazo compounds[13] and nitrogen as the ammonia radicle $N \equiv$ in the amines, amides, and nitriles. Here again, the relations are precisely expressed by polar structures for the nitrogen radicles without attendant indications of any tendencies towards ionization.

Nothing stated in this article is, however, to be interpreted to the effect that one radicle may not be converted into the electromeric one of opposite sign; but all such transformations represent explicit, easily recognized oxidation-reduction reactions.

Turning now to a further phase of this problem, we find that in the molecular rearrangements expressed in equations 1 and 2, the hypochlorous acid radicle of the chloroamine is converted into the common negative chloride ion of sodium chloride. According to the original Thomson theory of valence, in this change the positive chlorine atom of the chloroamine must capture two electrons from some other atom or atoms;

and, since the reagent used remains in the same condition of oxidation throughout the reaction, these electrons must be taken from some neighboring atom or atoms in the original molecule. This, obviously, must disturb the valences holding the atoms in the molecule, and a molecular rearrangement is altogether inevitable.

The evidence as to the charges on the individual atoms and radicles is clearest for triphenylmethylchloroamines and its analogs,[3] and we must formulate the rearrangement in the following way, the charges that are changed being indicated by heavy type:



$$(C_6H_5^+)_2{}^-_-\underset{(C_6H_5^+)}{C^+_-}{}^-\underset{\mathbf{Cl^+}}{N}{}^{\mathbf{-}}_{\mathbf{-}}{}^+H \xrightarrow{-H^{+-}Cl} (C_6H_5^+)_2{}^-_-\underset{(C_6H_5^+)}{C^+_{\mathbf{-}}}{}^-N \rightarrow (C_6H_5^+)_2{}^-_-C^+_{\mathbf{+}}{}^-N{}^{\mathbf{-}}_{\mathbf{-}}\;(C_6H_5^+) \rightarrow (C_6H_5^+)_2{}^-_-C^+_+{}^-_-N^-({}^+C_6H_5) \quad (3).$$

It is assumed that Cl^+ takes the two electrons first from the nitrogen originally holding it. (The same result would be obtained if the electrons were taken directly from the carbon by the positive chlorine. Evidence on this part of the problem is presented in the following article.) The nitrogen is thus rendered incapable of holding the H^+ and Cl^- and these are lost, forming sodium chloride and water with the reagent sodium hydroxide, as indicated in equation 2. The unsaturated (univalent[14]) nitrogen, in turn, takes two electrons from the carbon atom holding it, and the new positive charge produced thereby on the carbon atom must release one of the positive phenyl groups and this must move, under the force of the electrical field, to the negative nitrogen.

We recognize that the disturbing, labile element in the original structure is just the unstable, positive chlorine, so admirably represented by Thomson's first theory, and that its undeniably great tendency to go over into its common stable negative form is *the original source of the molecular disturbance and rearrangement.*

The product of the rearrangement, phenylimido benzophenone, in harmony with the electronic structure resulting for it according to equation 3, is uniformly hydrolyzed by acids to benzophenone and aniline:

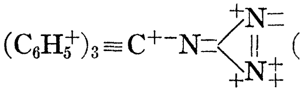
$$(C_6H_5)_2C^+_+{}^-_-N^-({}^+C_6H_5) + HOH + HCl \rightarrow (C_6H_5)_2C^+_+{}^-_-O + (C_6H_5^{+-}N{\equiv}H_3^+)^{+-}Cl \quad (4).$$

It is evident that the application of the original theory of Thomson to the valence relations in triphenylmethylchloroamine gives us a complete and precise picture of the cause, mode, and product of its molecular rearrangement.

If we attempt to express the rearrangement in terms of the theory that we may have non-polar, as well as polar valences existing simultaneously in molecules, we find the following: (1) It is necessary to assume polar valences in the chloroamine radicle, as was proved above. (2) We recognize the positively polarized chlorine as the unstable element in the molecule. (3) In the product, phenylimido benzophenone, we must assume at least partial polarization of the methylene carbon and nitrogen, in order to express precisely its mode of hydrolysis (equation 4). (4) It is necessary to assume therefore that at least one electron has migrated from the methyl carbon to the nitrogen (or chlorine). (5) To these definite conclusions may be added the fact that a presumptively negative group ^{-}OR attached to carbon never migrates[15] to nitrogen under these conditions, it is only presumably positive alkyl (CH_3^{+}) or alphyl ($C_6H_5^{+}$) radicles and hydrogen radicles H^{+} that migrate thus. In other words, so far as experiment penetrates into these molecular rearrangements, we find in the original molecule, in the reaction itself and in the product of the rearrangement evidences only of polar valences. The later modifications of the Thomson theory are of no assistance in formulating the theory of these reactions.

Finally, there is a whole group of rearrangements analogous to the rearrangement of chloroamines. In each instance one can plainly recognize, as the common characteristic of all the rearranging compounds, that the labile component in the original molecule is an unstable positive radicle or atom, which tends to go over into its stable negative form. In every instance, this tendency is found satisfied in the action, and as this involves the absorption of electrons from neighboring atoms in the original molecule, one must conclude that in all of these cases the tendency mentioned and its satisfaction bring about the rearrangement. These relations hold for the following groups of compounds:

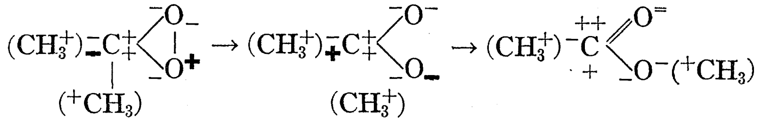
1. *Hydroxylamine* derivatives, such as $(C_6H_5)_3C.HN^{-+}OH$ (considered in the following article), in which the positive hydroxide group[12] is unstable, tending to form the well known negative group. The molecular rearrangement may be expressed[12] by the same equation 3 as was used for the chloroamine, if ^{+}OH is substituted for Cl^{+} and HO^{-} for Cl^{-}.



2. *Azides*, such as $(C_6H_5^{+})_3{\equiv}C^{+-}N{=}\left<\begin{matrix}^{+}N{=}\\ \Vert\\ {}_{+}N^{+}_{+}\end{matrix}\right.$ (see the following article), which tend to lose the neutral molecule N_2 with a gain of two electrons for the radicle N_2^{++}. Again equation 3 may be used to express the whole action, the loss of N_2 being substituted for the loss of HCl. (The azide is formed by the action of nitrous acid $N^{++}_{+}{=}O(^{-}OH)$ on the hydrazine $(C_6H_5)_3C.HN^{-+}NH_2$,[16] which leads to the structure used.

The same net result would be shown if the alternative structure[17] $(C_6H_5)_3C^{+-}N\overset{-}{=}(^{++}N^{+++})\equiv N$ were accepted for the azide.)

3. *Peroxides*, in whose rearrangement a positive charge on an oxygen atom is converted into a stable negative charge:


(5).

In conclusion, the effects of an electric current in decomposing the salts of organic acids are entirely analogous, fundamentally, to these molecular rearrangements.[12] With the current the effect is produced by the positive electrode charge, with these compounds, by the positive polar charges on the specific atoms, as just shown.

The original Thomson theory of electron valences is evidently extremely useful in the precise formulation of these molecular rearrangements, involving a large group of organic reactions. Of the newer theories of Thomson, Bray and Branch, and Lewis, we find occasion to use only so much as is already found in the original theory. This, of course, does not exclude the possibility that the newer assumptions may reveal their usefulness in other fields of investigation. (Thomson's structure for benzene, developed on the basis of the newer theory,[18] interpreted rigorously and without further limiting assumptions, seems to make possible at least *four* di-substitution products C_6H_4XY, while only the *three* well known series have been recognized.)

(For references see end of following article.)

MOLECULAR REARRANGEMENTS OF TRIPHENYLMETHANE DERIVATIVES. II. EXPERIMENTAL PART

By Julius Stieglitz and Collaborators

KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO

Read before the Academy, December 9, 1914. Received, February 20, 1915

MOLECULAR REARRANGEMENTS OF TRIPHENYLMETHYL HALOGEN AMINES[5]

WITH ISABELLE VOSBURGH † AND AGNES FAY MORGAN

The study of the mechanism of the molecular rearrangement of acyl halogen amines RCO.NH(Hal) is complicated by the fact that the salts formed by the bases used as reagents to start the rearrangement may

---

† My young collaborator, Miss Vosburgh, who carried out the first part of the experimental work of this investigation most skilfully and conscientiously, died December 4, 1914, as the result of an automobile accident.—J. S.